



**SEMMELWEIS UNIVERSITY**

Lágy Anyagok  
Laboratóriuma

Dept. of Biophysics and Radiation Biology,  
Laboratory of Nanochemistry

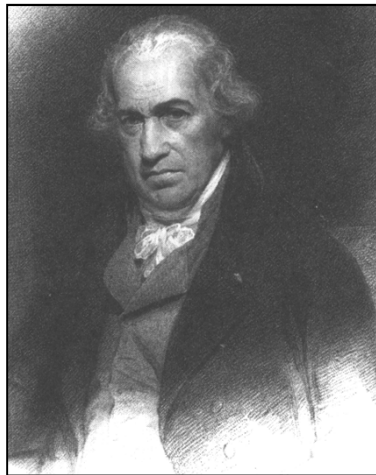
# **THERMODYNAMICS**

**Miklós Zrínyi**

*[mikloszrinyi@gmail.com](mailto:mikloszrinyi@gmail.com)*

# What is thermodynamics?

- *Classical definition*: branch of physics studying the effects of changes in temperature, pressure and volume (energy changes).
- *Therme* (Gr) heat, *dynamis* (Gr) power.



*James Watt (1736-1819)*



$$\Delta U = \Delta Q + \Delta W$$



# Thermodynamics

"Classical thermodynamics... is the only physical theory of universal content concerning which I am convinced that, within the framework of applicability of its basic contents, will never be overthrown."

*-Albert Einstein*

- It reveals the driving forces behind natural phenomena.
- Due to its generalizations, it has abstract, complex and difficult-to-understand concepts.

"Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by that time you are so used to it, it doesn't bother you any more."

*-Arnold Sommerfeld*

- Classical thermodynamics, which was developed in the first half of the nineteenth century by Carnot, Clausius, Joule, Kelvin, and Mayer (and others), is a *phenomenological* theory, dealing with macroscopic phenomena, and avoiding atomic concepts.
- Its strength lies in the generality of its predictions, which are based on the small number postulates set out in the laws of thermodynamics, and apply to all macroscopic systems; e.g. solids, fluids and electromagnetic radiation.

Its weakness also lies in great generality, since it cannot be applied to real systems without auxiliary input, either experimental or theoretical.

For example: the equation of state of a fluid, linking pressure, volume and temperature, must be derived from experiment.

<u>École Polytechnique</u>	<u>Glasgow school</u>	<u>Berlin school</u>	<u>Edinburgh school</u>
			
<u>Sadi Carnot</u> (1796-1832)	<u>William Thomson</u> (1824-1907)	<u>Rudolf Clausius</u> (1822-1888)	<u>James Maxwell</u> (1831-1879)
<u>Vienna school</u>	<u>Gibbsian school</u>	<u>Dresden school</u>	<u>Dutch school</u>
			
<u>Ludwig Boltzmann</u> (1844-1906)	<u>Willard Gibbs</u> (1839-1903)	<u>Gustav Zeuner</u> (1828-1907)	<u>Johannes der Waals</u> (1837-1923)

- Temperature and heat are different.  
(**Joseph Black**)
- First thermometer  
(**Galileo Galilei**)
- First clinical thermometer  
(**Jean Rey 1631**)
- Early temperature scale  
(**Anders Celsius 1742**).
- Temperature scale  
(**Carl von Linne**)



$$F = 1.8C + 32$$

$$K = C + 273.15$$

Fahrenheit: water freezes at 32 °F; boils at 212 °F

Celsius: water freezes at 0 °C; boils at 100 °C

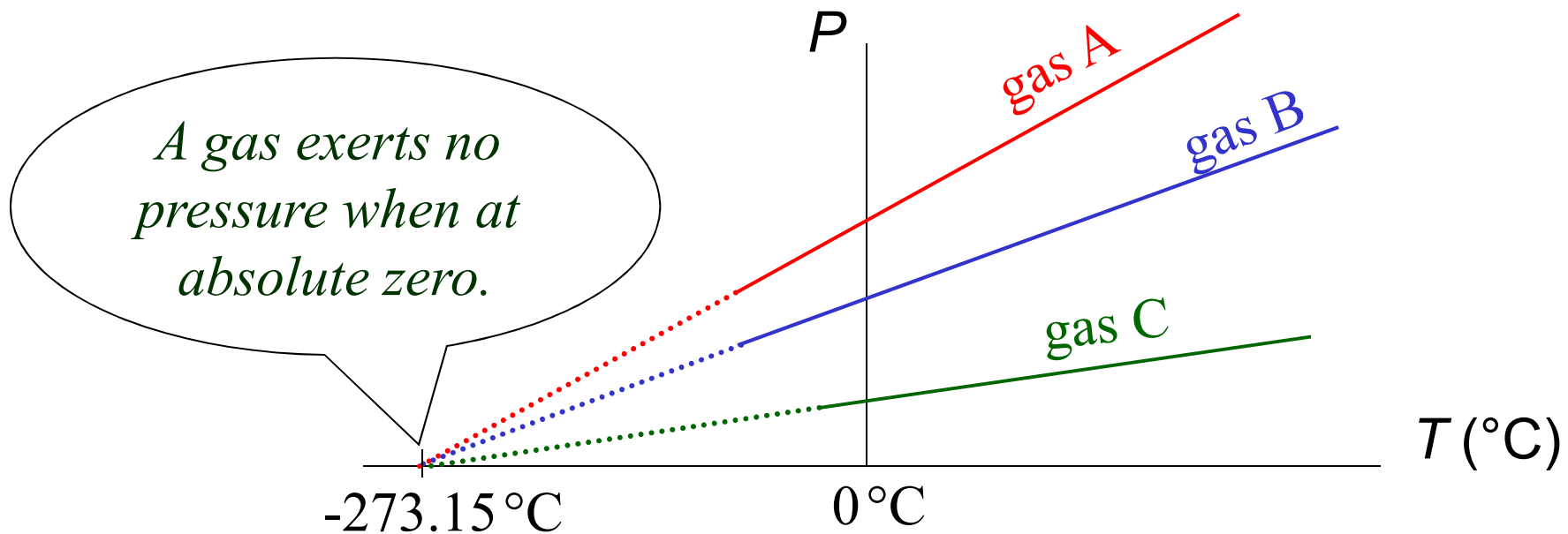
Kelvin: water freezes at 273.15 K; boils at 373.15 K

$$F = 1.8C + 32$$

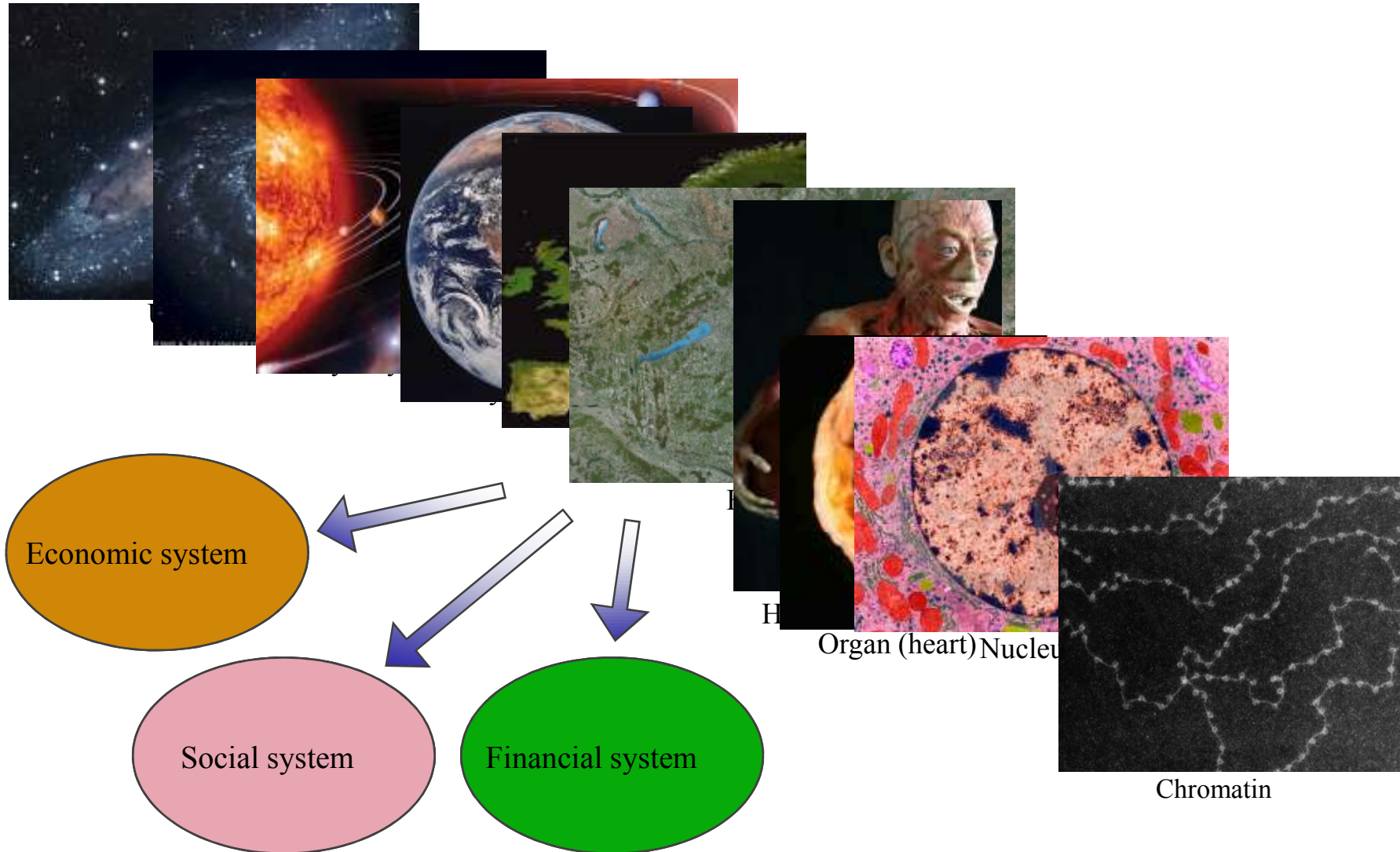
$$K = C + 273.15$$



**The Kelvin scale** is setup so that its zero point is the coldest possible temperature--absolute zero, at which point a substance would have zero internal energy. This is  $-273.15^{\circ}\text{C}$ . Absolute zero can never be reached, but there is no limit to how close we can get to it. Scientists have cooled substances to within  $10^{-5}$  kelvins of absolute zero. How do we know how cold absolute zero is, if nothing has ever been at that temperature?

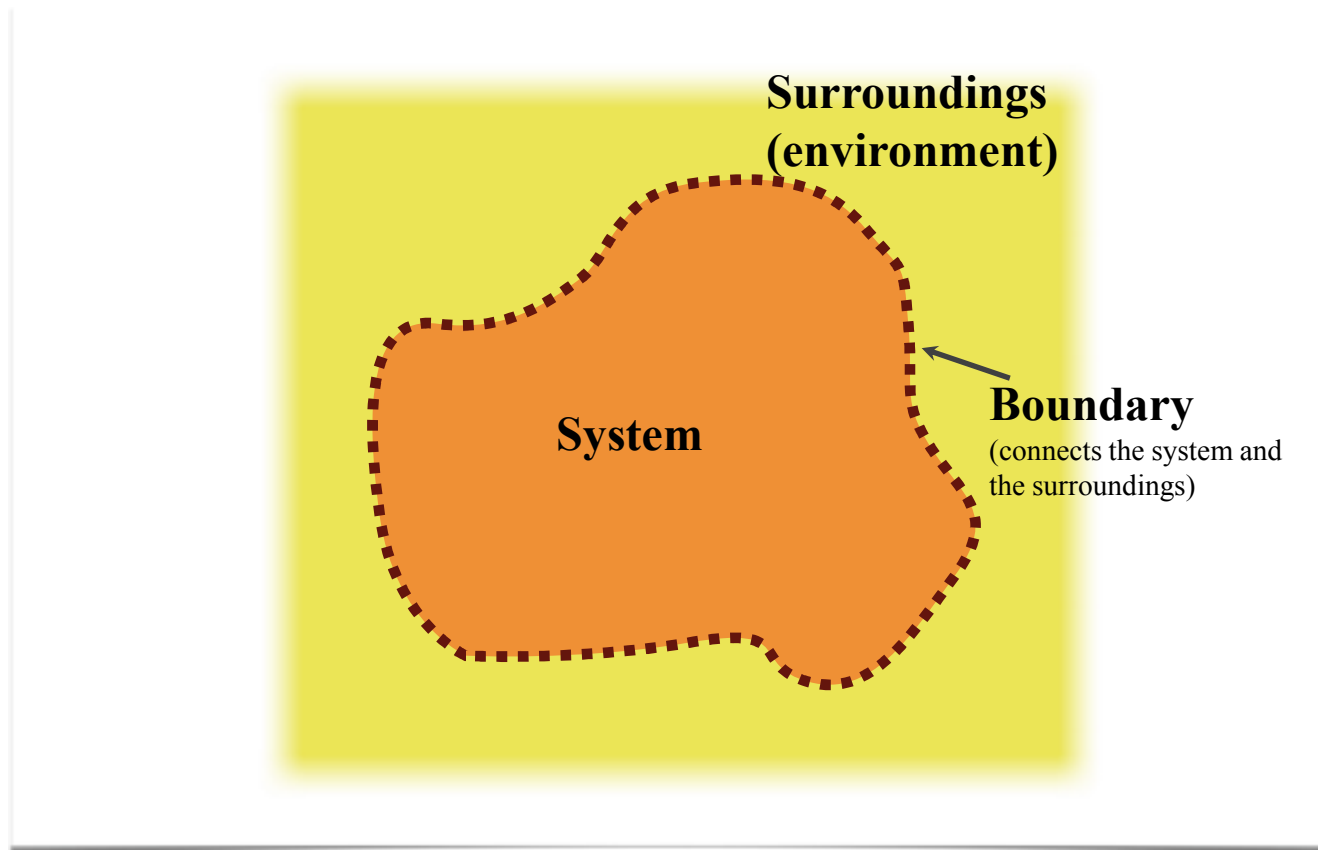


# Thermodynamic system today



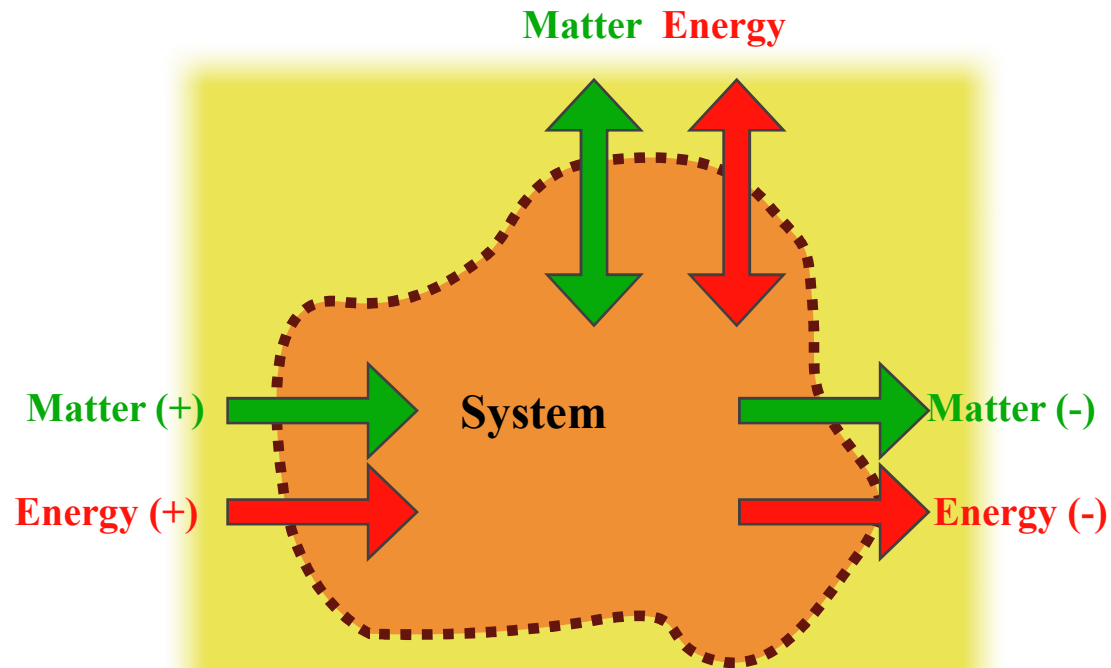
# Abstraction of the thermodynamic system

*Definition:* the thermodynamic system is the part of nature under investigation.



# The thermodynamic system interacts with the surroundings

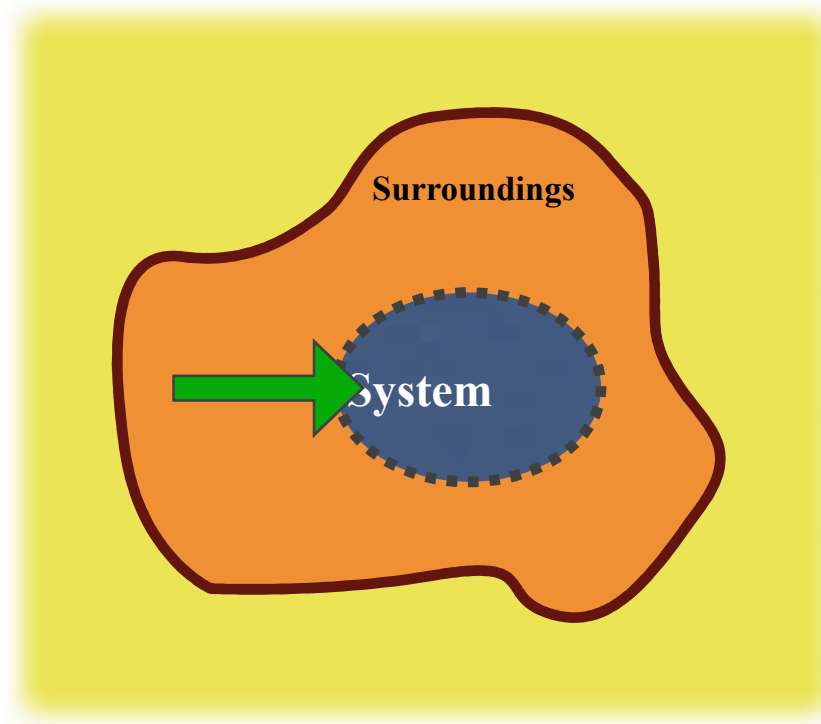
Exchange of matter and energy may occur across the boundary.



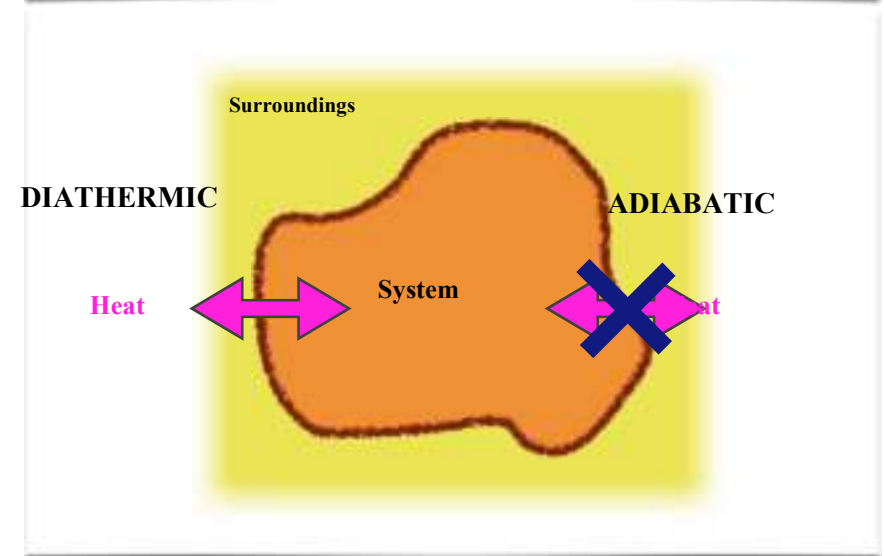
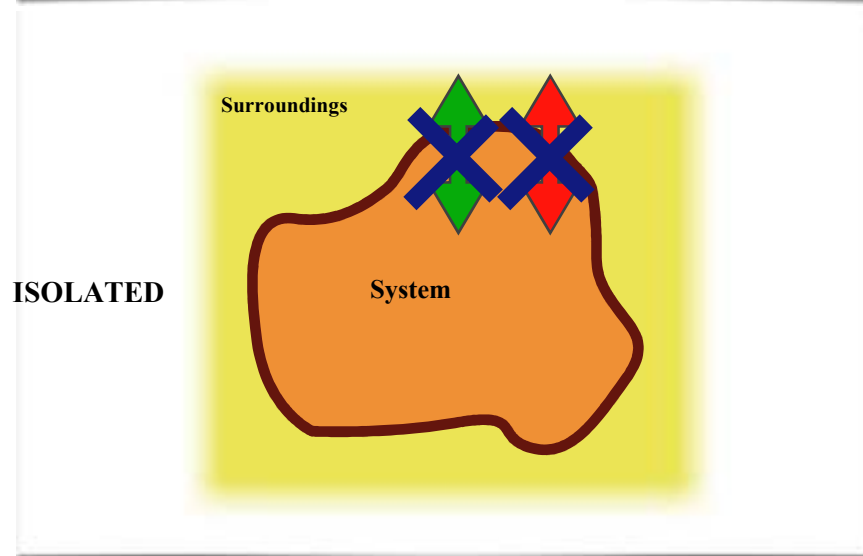
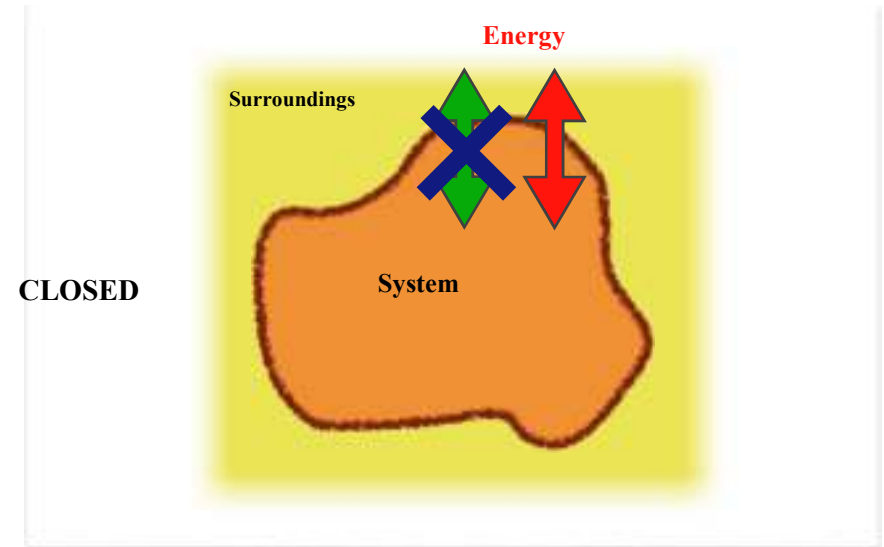
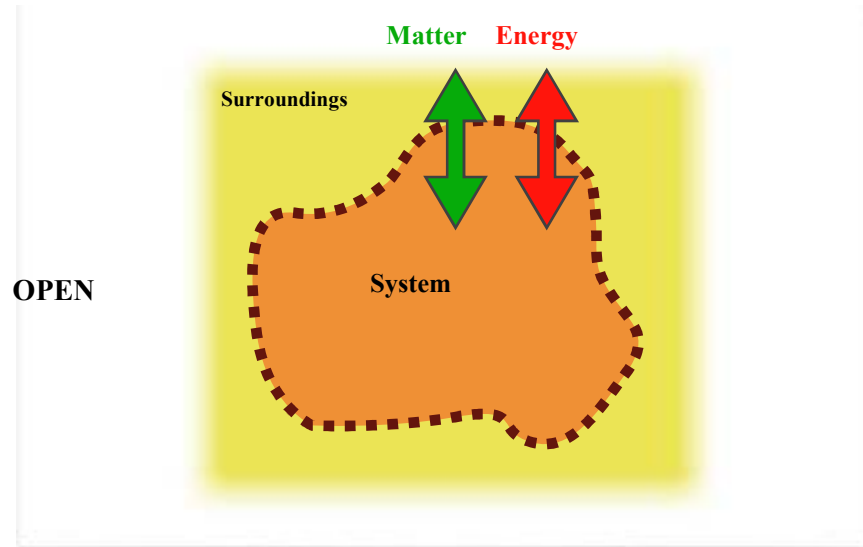
*Sign convention!*

# The thermodynamic system interacts with the surroundings

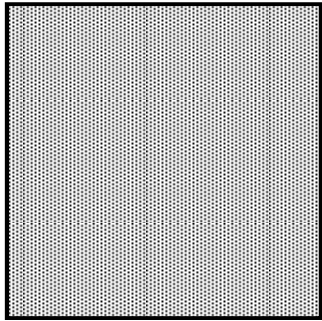
Defining the thermodynamic system has consequences for processes.



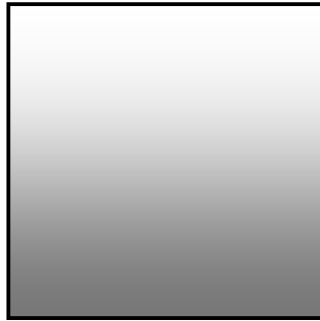
# Types of thermodynamic systems



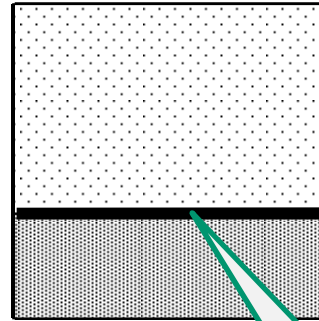
## Types of thermodynamic systems



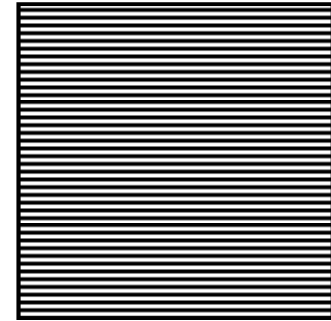
***Homogeneous  
uniform***



***inhomogeneous***



***heterogen***



***anisotropic***

*interface*

# Characterization of the thermodynamic system

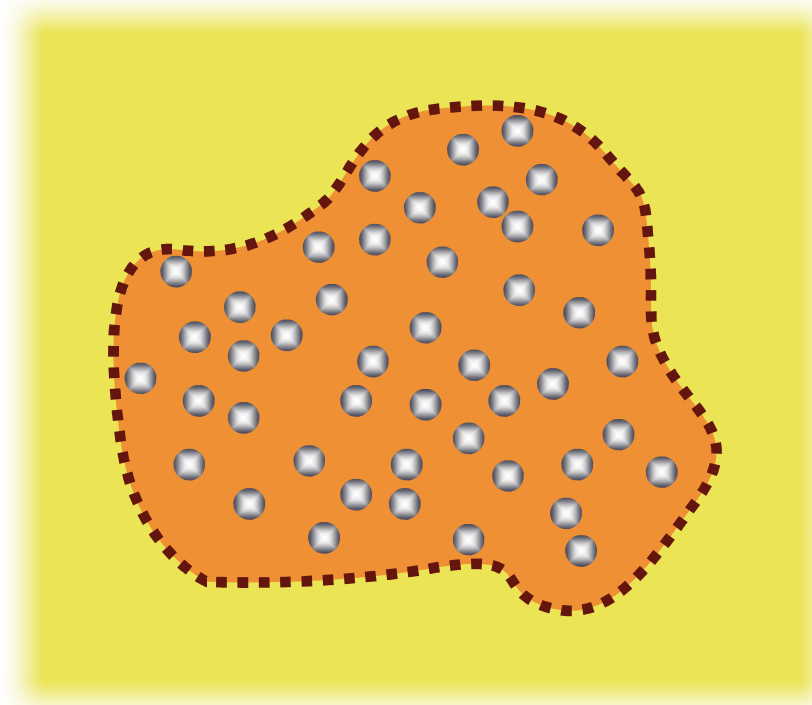
Macroscopic characterization: **state variables**  
- explicitly determine the *state* of the system.

Pressure:  $p$

Volume:  $V$

Temperature:  $T$

Concentration:  $c$



Universal gas law

$$pV=nRT$$



## Isolated, Closed and Open Systems

- A ***system*** is the portion of the physical world being studied.
- The system plus surroundings comprise a ***universe***.
- The boundary between a system and its surroundings is the ***system wall***.
- If heat cannot pass through the system wall, it is termed an ***adiabatic wall***, and the system is said to be ***thermally isolated*** or ***thermally insulated***.
- If heat can pass through the wall, it is termed a ***diathermal wall***.
- Two systems connected by a diathermal wall are said to be in ***thermal contact***.

## Isolated, Closed and Open Systems

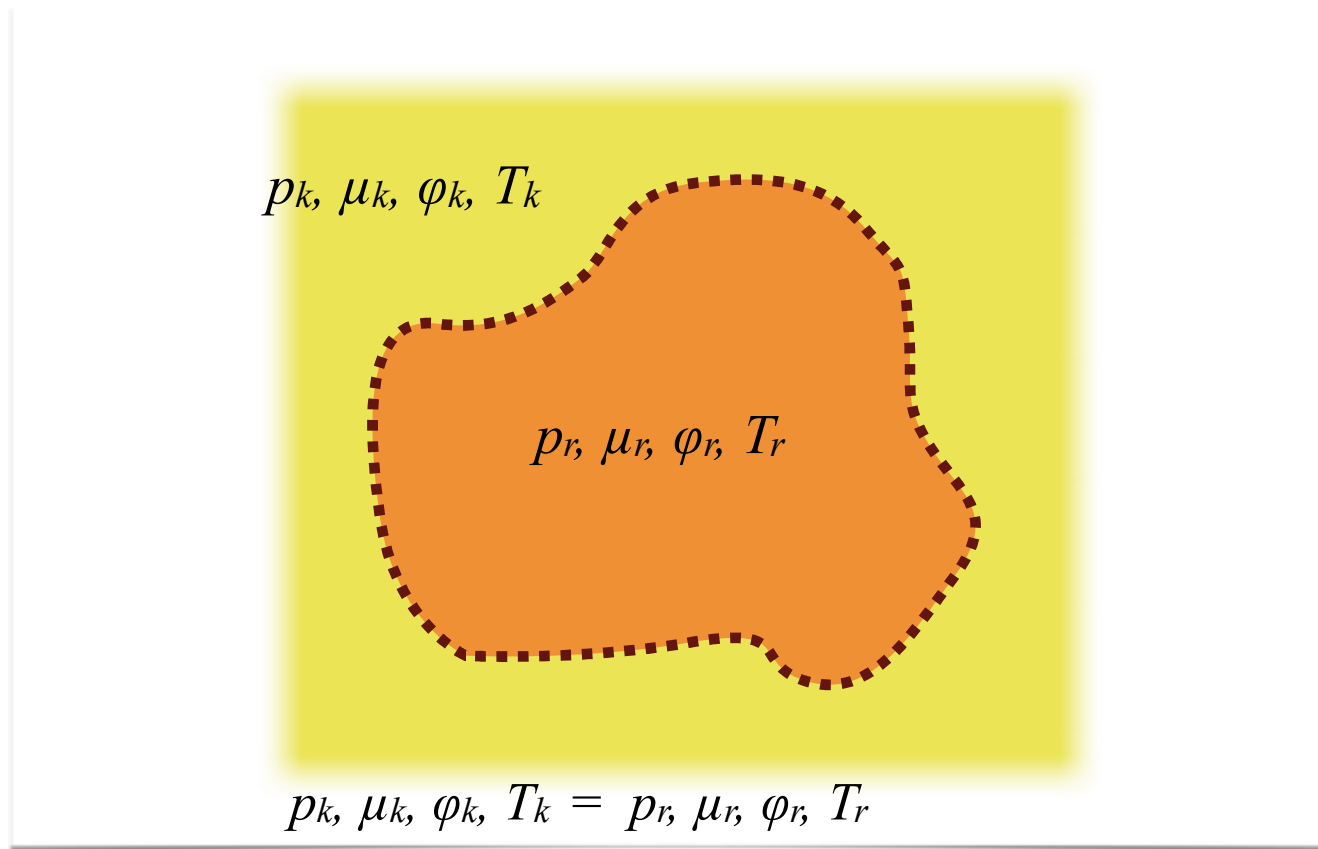
- An ***isolated system*** cannot exchange mass or energy with its surroundings.
- The wall of an isolated system must be adiabatic.
- A ***closed system*** can exchange energy, but not mass, with its surroundings.
- The energy exchange may be mechanical (associated with a volume change) or thermal (associated with heat transfer through a diathermal wall).
- An ***open system*** can exchange both mass and energy with its surroundings.

## Thermodynamic Variables

- *Thermodynamic variables* are the observable macroscopic variables of a system, such as P, V and T.
- If they are used to describe an equilibrium state of the system, they are known as *state variables*.
- *Extensive variables* depend on the size of the system; e.g. mass, volume, entropy, magnetic moment.
- *Intensive variables* do not depend on size; e.g. pressure, temperature, magnetic field.
- An extensive variable may be changed to an intensive variable, known as a *specific value*, by dividing it by a suitable extensive variable, such as mass, no. of kmols, or no. of molecules.
- Example: the specific heat is normally (heat capacity)/(mass).

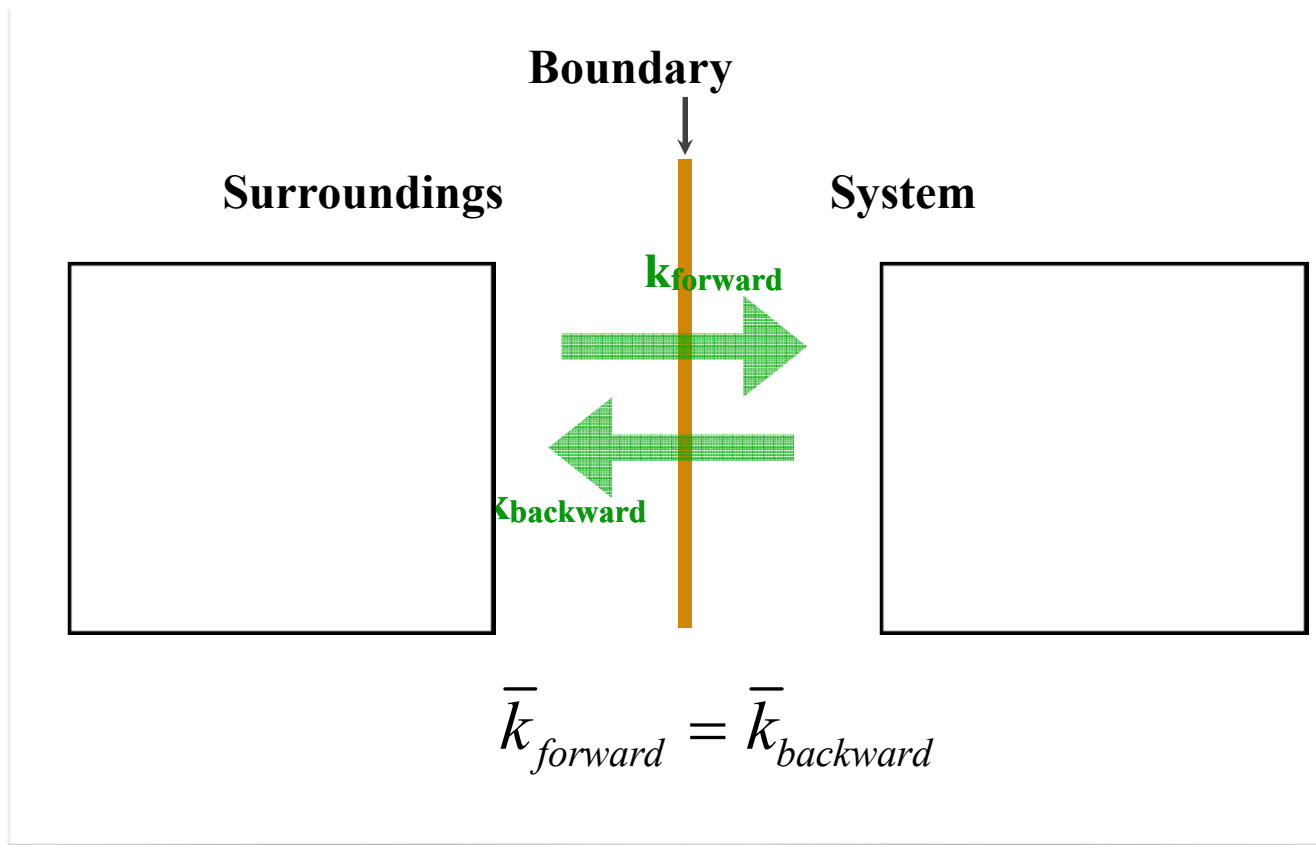
# Equilibrium

*Macroscopic description:* intensive variables are identical (between the system and surroundings, or between different parts of the system)



# Equilibrium

*Microscopic description:* average rates of forward and reverse reactions are equal.

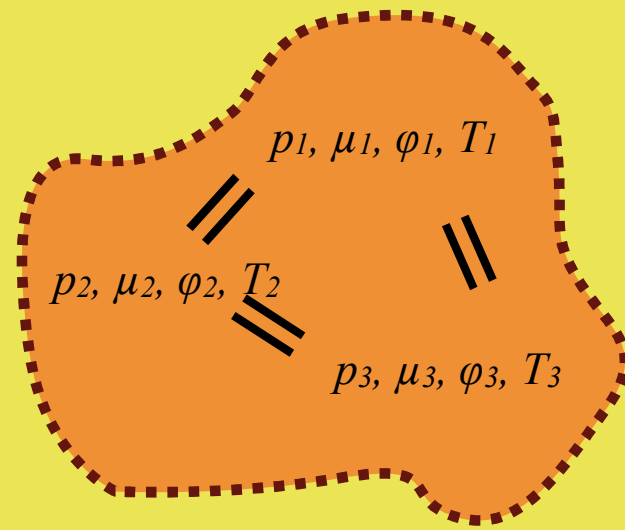
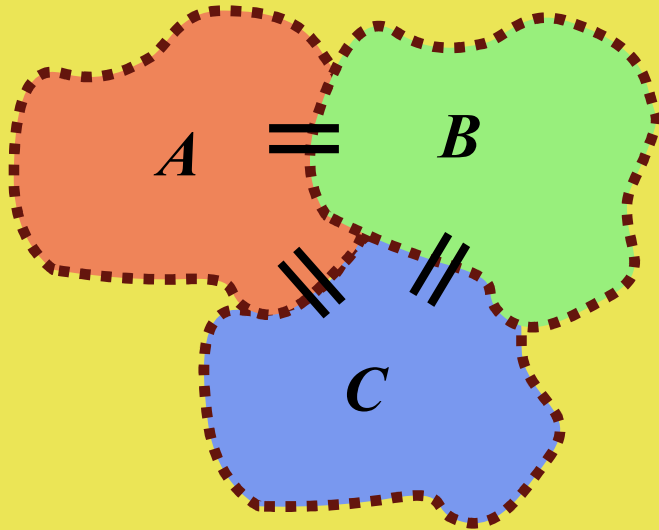


# Equilibrium States

- An *equilibrium state* is one in which the properties of the system do not change with time.
- In many cases, an equilibrium state has intensive variables which are uniform throughout the system.
- A *non-equilibrium state* may contain intensive variables which vary in space and/or time.
- An *equation of state* is a functional relationship between the state variables; e.g. if  $P, V$  and  $T$  are the state variables, then the equation of state has the form  $f(P, V, T) = 0$ .
- In 3-dimensional  $P$ - $V$ - $T$  space,
  - an equilibrium state is represented by a point,
  - and the equation of state is represented by a surface.

# Zeroth law of thermodynamics

- If two systems ( $A$  and  $B$ ) are independently in equilibrium with a third one ( $C$ ), then they are in equilibrium with each other as well.
- Between different points of a system in equilibrium, the intensive variables are equal (there are no thermodynamic currents).

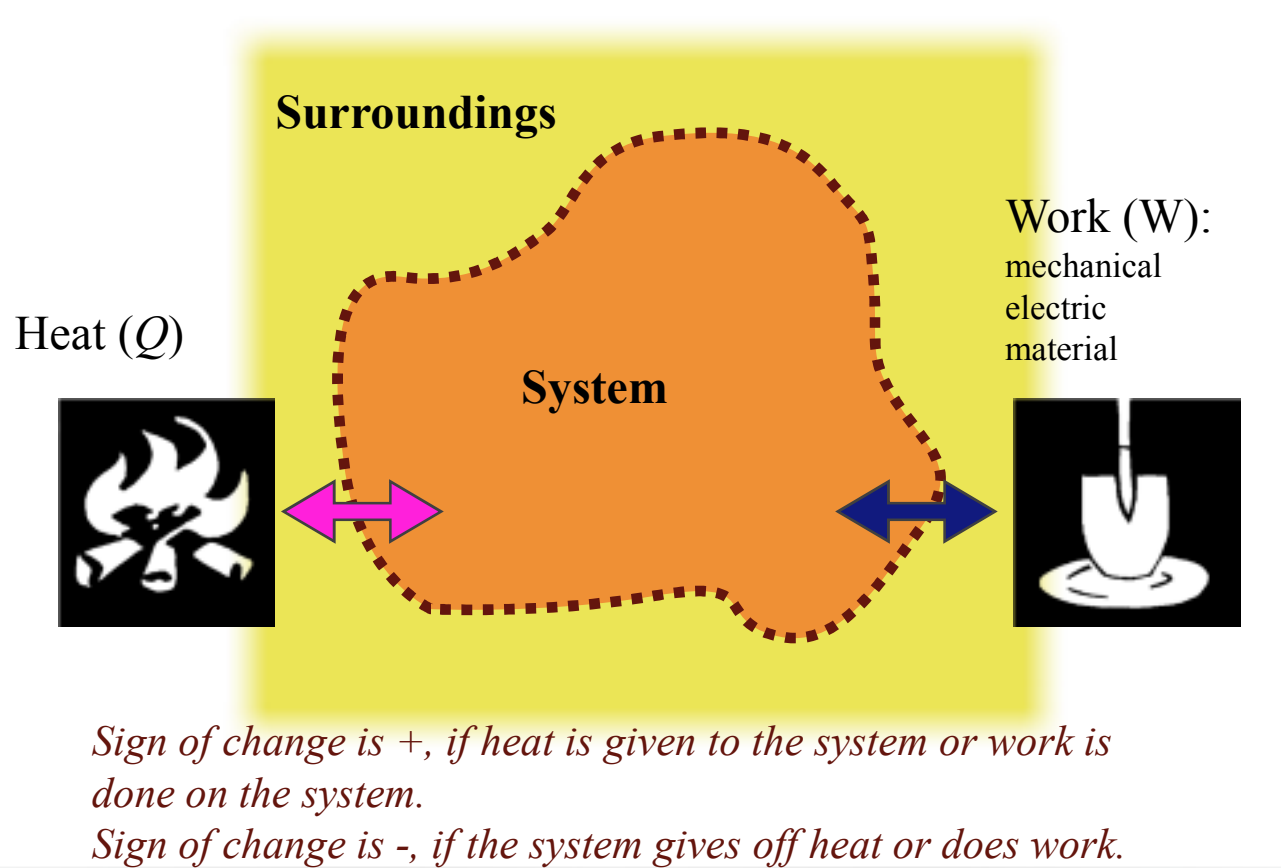


# Change

Thermodynamics is interested in the changes within the system.

Changes may be evoked by: heating, work.

Result: **internal energy of the system changes.**





# Thermodynamic processes

- *Isobaric*: at constant pressure.
- *Isochoric (isometric, isovolumetric)*: at constant volume.
- *Isothermic*: at constant temperature.
- *Adiabatic*: no heat exchange.
- *Isentropic*: at constant entropy.
- *Isenthalpic*: at constant enthalpy.
- *"Steady state"*: at constant internal energy.

# Processes 1

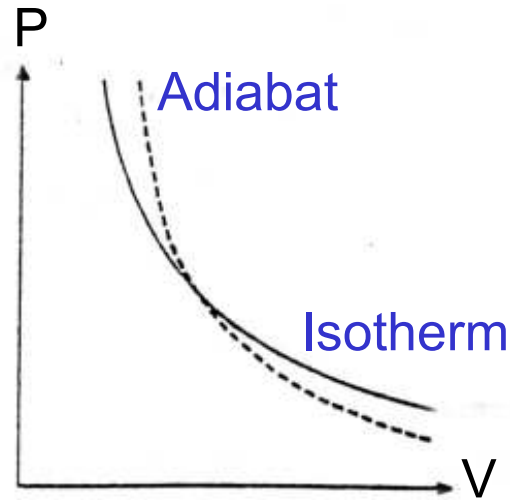
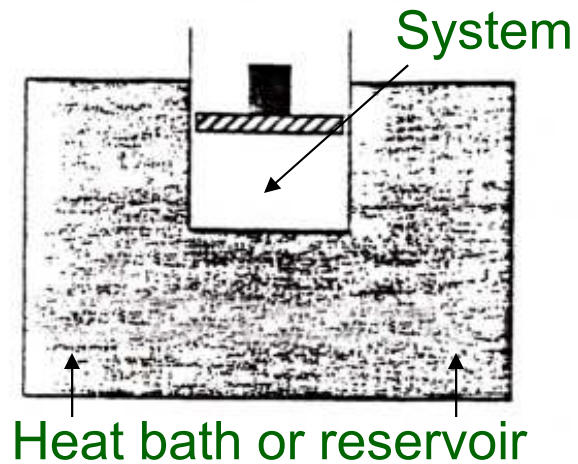
- A *process* refers to the change of a system from one equilibrium state to another.
- The initial and final states of a process are its *end-points*.
- A *quasistatic process* is one that takes place so slowly that the system may be considered as passing through a succession of equilibrium states.
- A quasistatic process may be represented by a *path* (or line) on the equation-of-state surface.
- If it is *non-quasistatic*, only the end-points can be shown.
- A *reversible process* is one the direction can be reversed by an infinitesimal change of variable.
- A reversible process is a quasistatic process in which no dissipative forces, such as friction, are present.
- A reversible change must be quasistatic, but a quasistatic process need not be reversible; e.g. if there is hysteresis.

# Processes 2

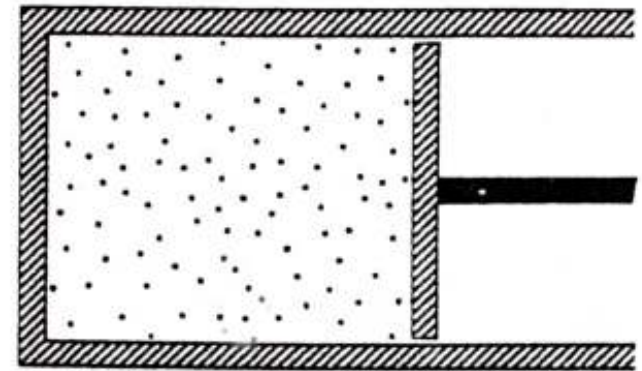
- An *isobaric* process is one in which the pressure is constant.
- An *isochoric* process is one in which the volume is constant.
- An *isothermal* process is one in which the temperature is constant.
- An *adiabatic* process is one in which no heat enters or leaves the system; i.e.  $Q = 0$ .
- If a system is left to itself after undergoing a non-quasistatic process, it will reach equilibrium after a time  $t$  much longer than the longest relaxation time  $\tau$  involved; i.e.  $t \gg \tau$ .
- *Metastable equilibrium* occurs when one particular relaxation time  $\tau_0$  is much longer than the time  $\Delta t$  for which the system is observed; i.e.  $\tau_0 \gg \Delta t$ .

# Three Types of Process

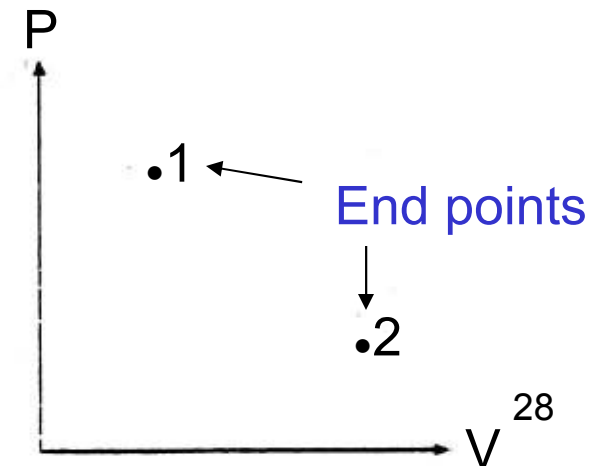
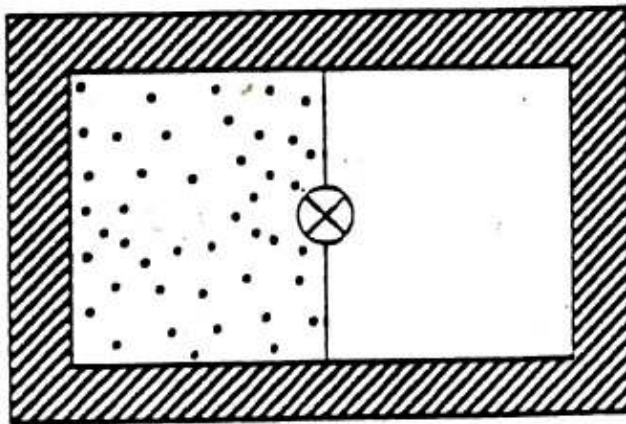
## Isothermal process



## Adiabatic process



## Adiabatic free expansion



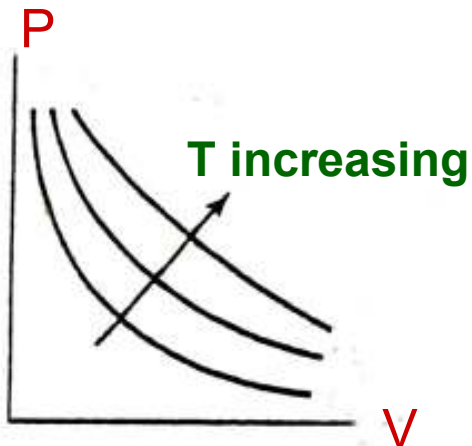
# The Ideal Gas Law

- Ideal gas law  $PV = nRT$  or  $PV_m = RT$ ,
- where  $n$  is the no. of kmoles,  $v$  is the volume per kmole,  $T$  is the absolute temperature in K, and the gas constant  $R = 8.314 \times 10^3 \text{ J/(K.kmol)}$ .
- For a constant quantity of gas,  $P_1V_1/T_1 = P_2V_2/T_2$ .

## Boyle's Law

$$P_1V_1 = P_2V_2$$

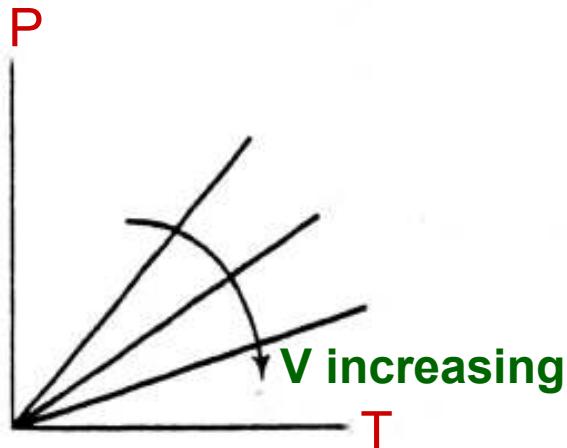
( $T$  constant)



## Gay-Lussac Law

$$P_1/T_1 = P_2/T_2$$

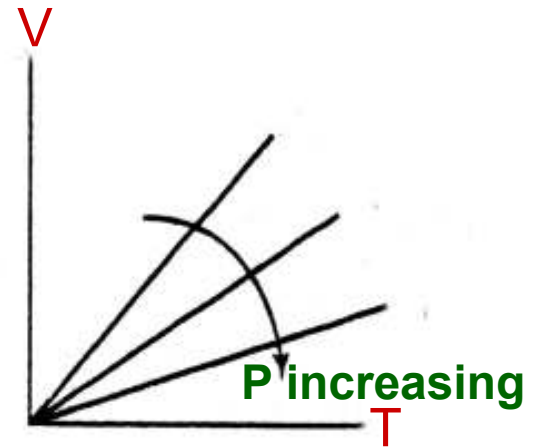
( $V$  constant)



## Charles' Law

$$V_1/T_1 = V_2/T_2$$

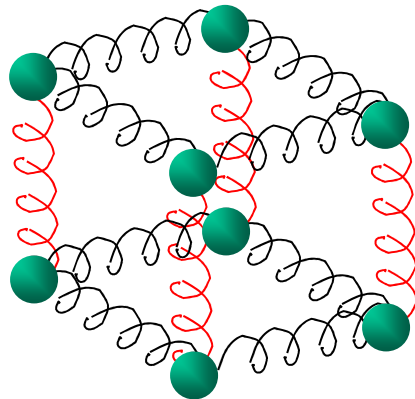
( $P$  constant)



## Internal energy

Internal energy is the energy an object or substance is due to the molecular **kinetic** and **potential** energies associated with the random motions of all the particles that make it up.

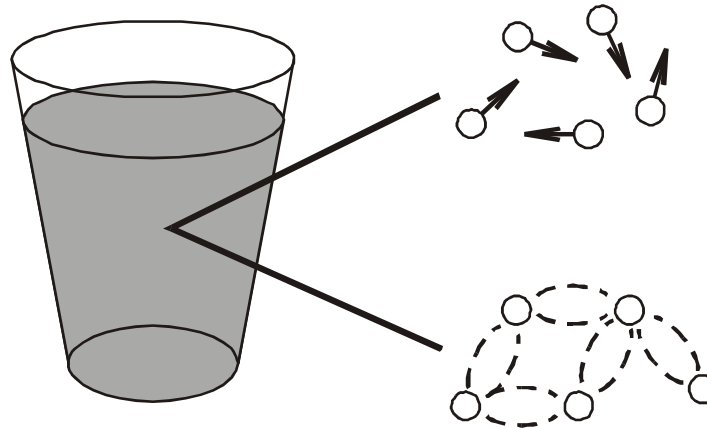
The kinetic energy is due to the motion of the particles. The potential energy is due to interactions between atoms, ions and molecules.



$$E = E_{pot} + E_{kin} + U$$

Microscopic characterization: **internal energy ( $U$ )**

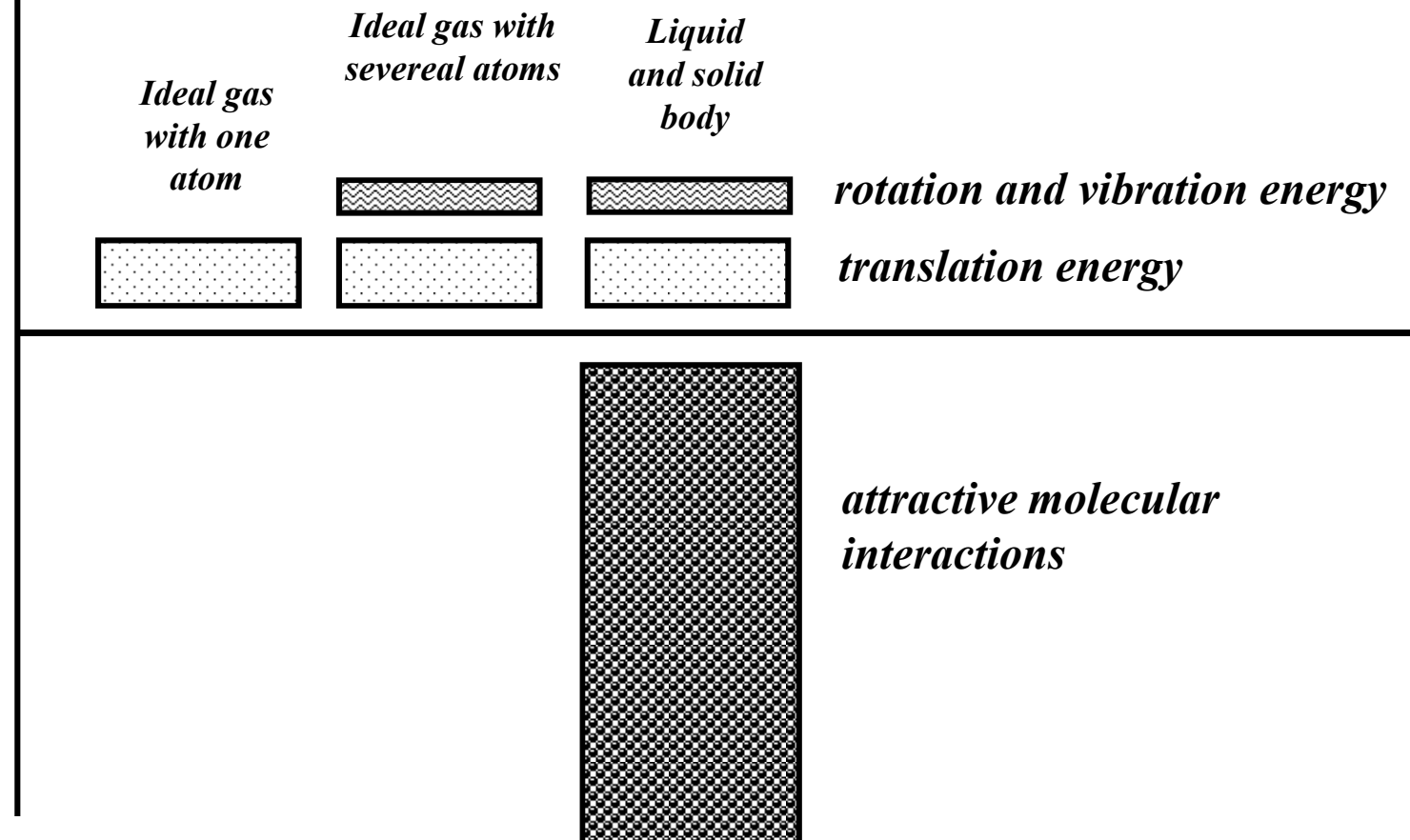
**Macroscopic**  
potential- and  
kinetic energies  
are not included  
in the internal  
energy.



**Molecular**  
potential- and  
kinetic energies  
are in the internal  
energy.

*Internal energy does not contain the potential  
and kinetic energy of the macroscopic body.*

***Standard internal energy (298 K)***





The **van der Waals force** is the attractive force between molecules (or between parts of the same molecule) other than those due to covalent bonds or to the electrostatic interaction of ions with one another or with neutral molecules. The term includes interactions of:

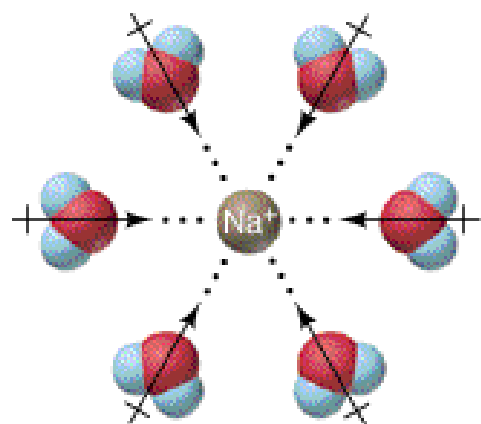
- ion – permanent dipole
- ion – induced dipole
- permanent dipole – permanent dipole
- permanent dipole – induced dipole
- instantaneous induced dipole-induced dipole
- H bond
- *hydrophobic*

Van der Waals forces are **relatively weak** compared to normal chemical bonds, but play a fundamental role

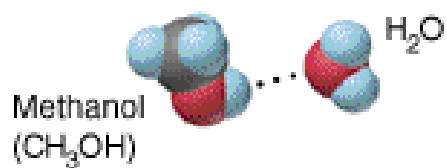


## Dipole – charge interaction

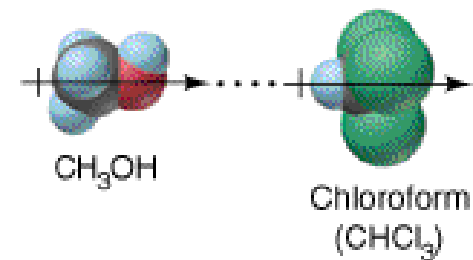




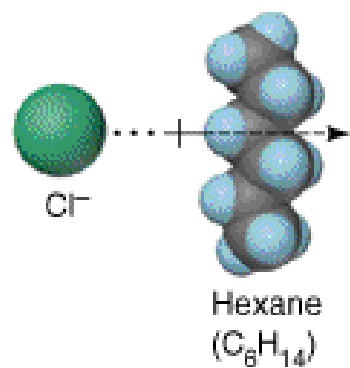
Ion-dipole



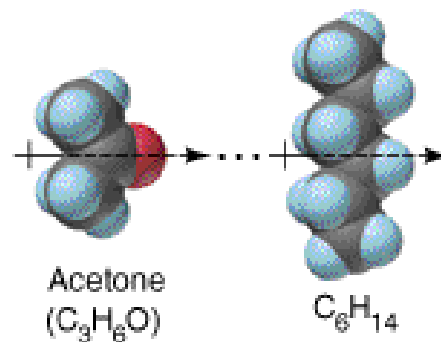
H bond



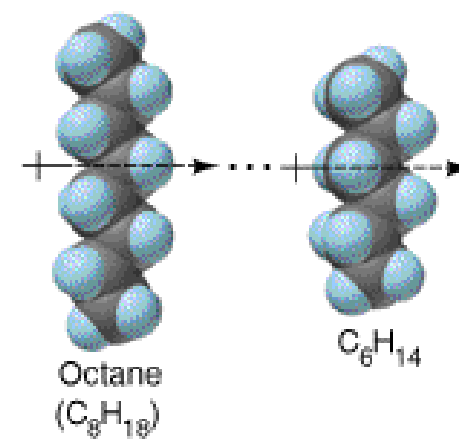
Dipole-dipole



Ion-induced dipole



Dipole-induced dipole



Dispersion

$\epsilon_o$ 

Permittivity of vacuo:  $\epsilon_o$

Relative permittivity:  $\epsilon_r$

Energy of ionization:  $I$

Distance between molecules:  $r$

ion-ion

$$\left( \frac{1}{4\pi\epsilon_0\epsilon_{rel}} \right) \cdot \frac{q_1 q_2}{r}$$

ion-dipole

$$-\left( \frac{1}{4\pi\epsilon_0} \right)^2 \frac{\mu_1 q_2}{r^2}$$

dipole-dipole

$$-\left( \frac{1}{4\pi\epsilon_0} \right)^2 \cdot \frac{2}{3k_B T} \cdot \frac{\mu_1^2 \mu_2^2}{r^6}$$

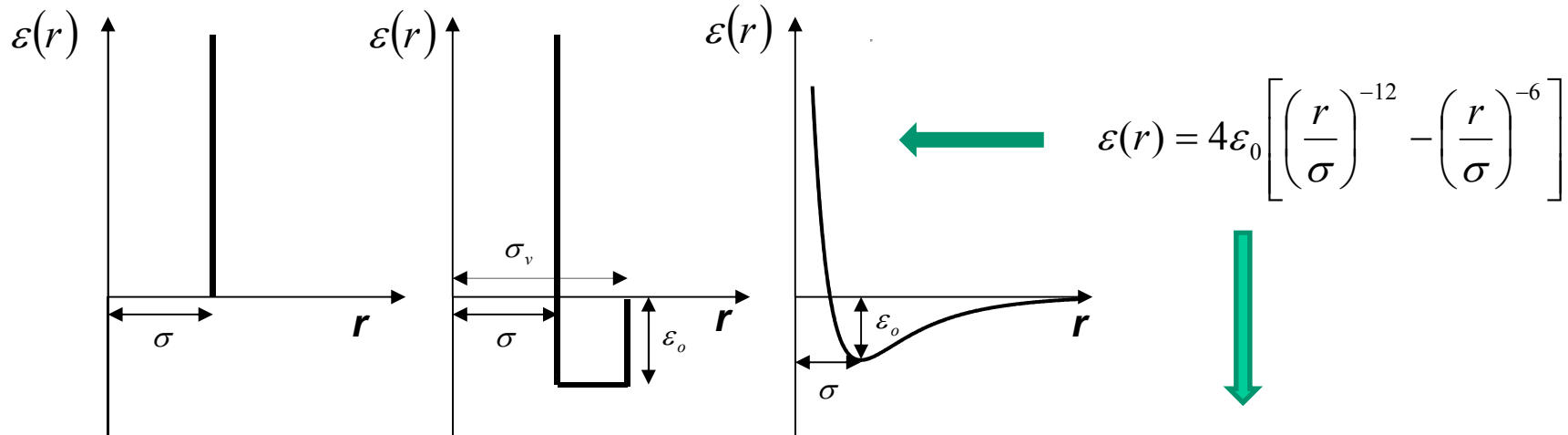
induced dipole-dipole

$$-\left( \frac{1}{4\pi\epsilon_0} \right)^2 \cdot \frac{\mu_1^2 \alpha_2}{r^6}$$

induced dipole-induced dipole

$$-\left( \frac{1}{4\pi\epsilon_0} \right)^2 \cdot \frac{3}{2} \cdot \frac{I_1 I_2}{I_1 + I_2} \frac{\alpha_1 \alpha_2}{r^6}$$

# Modelling molecular interactions



$$\begin{aligned}
 U = & \sum_{i < j} \sum 4\varepsilon_0 \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \\
 & + \sum_{i < j} \sum \frac{q_i q_j}{4\pi\epsilon_0 r_{ij}} \\
 & + \sum_{\text{bonds}} \frac{1}{2} k_s (r - r_0)^2 \\
 & + \sum_{\text{angles}} \frac{1}{2} k_\theta (\theta - \theta_0)^2 \\
 & + \sum_{\text{torsions}} k_\phi [1 + \cos(n\phi - \delta)]
 \end{aligned}$$

The diagrams illustrate the physical meaning of the terms in the potential energy equation:

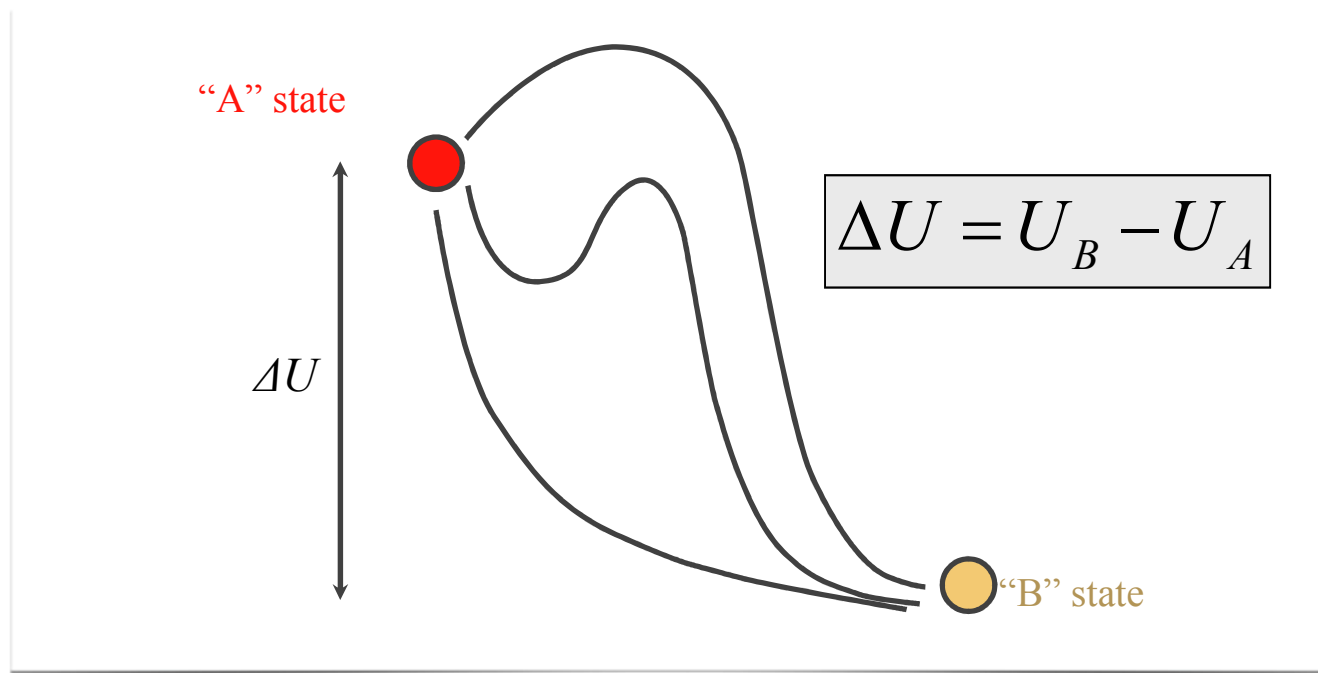
- Pair potential:** A graph of  $U$  vs  $r$  showing a minimum at  $r = \sigma$  with depth  $\varepsilon$ .
- Electrostatic interaction:** A diagram showing a red sphere (charge  $q_i$ ) and a blue sphere (charge  $q_j$ ) at distance  $r$ .
- Bond stretching:** A diagram showing two spheres connected by a spring with equilibrium distance  $r_0$ .
- Angle bending:** A diagram showing three spheres forming an angle  $\theta$  with equilibrium angle  $\theta_0$ .
- Torsion:** A diagram showing a chain of four spheres with a torsional angle  $\phi$  and equilibrium angle  $\delta$ .

Interaction	Energy in RT units
<i>chemical reaction</i>	40 - 200
<i>ion-ion</i>	80 - 100
<i>ion – dipole</i>	10 - 20
<i>H-bond</i>	10 - 15
<i>dipole –dipole</i>	0,5 - 2
<i>induced dipole –dipole</i>	0,3 - 2
<i>induced dipole – induced dipole</i>	0,2 - 2

# Internal energy (U) is “state function”

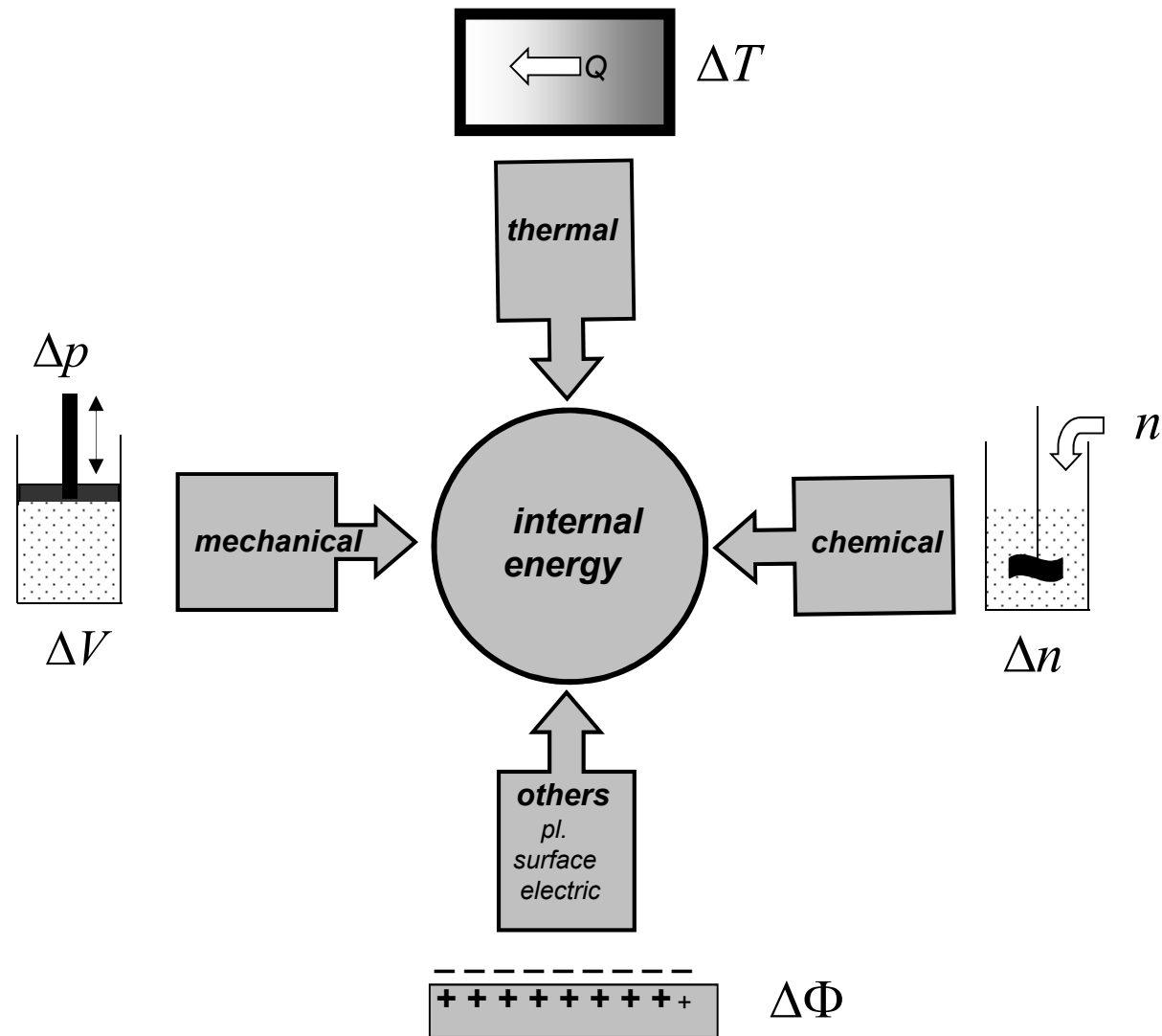
**State functions:** single-value functions of the state variables (independent variables) of the system.

Change in the state functions depend only on the initial and final states of the system; it is independent of the path.



Other state functions: enthalpy (H), Helmholtz free energy (F), Gibbs free energy (G), entropy (S)

# Change of internal energy

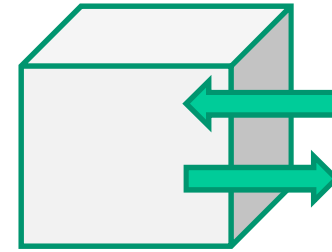




# Change in internal energy

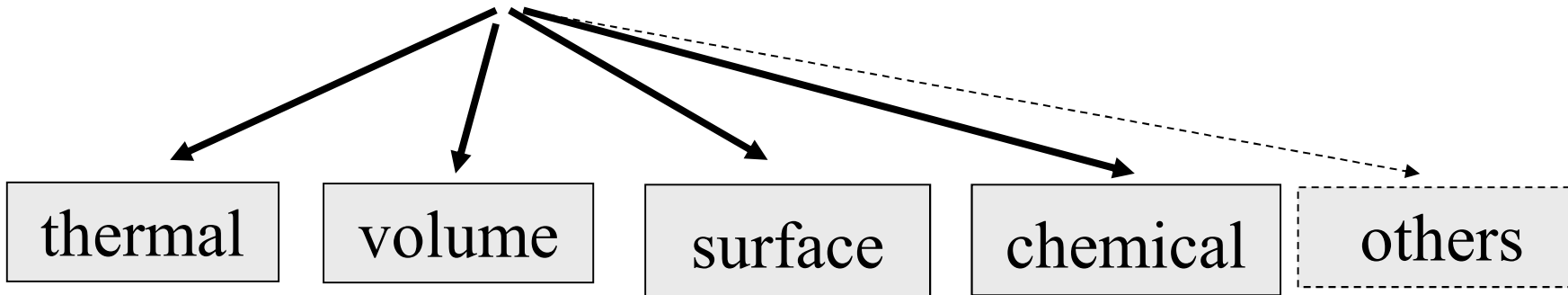


## *Elementary energy exchanges*



$$\Delta X > 0$$

$$\Delta X < 0$$

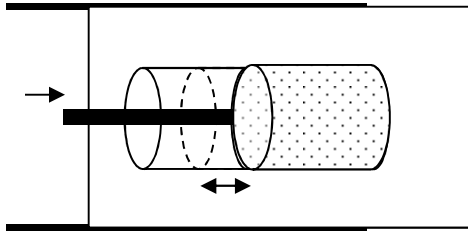


The change of internal energy is the sum of individual energy exchanges

$$\Delta U = \Delta Q + \sum_i \Delta W_i$$

## *Mechanical interactions (1)*

- *mechanikai work*



$$dW_{mech} = -f(x) \cdot dx$$

$$W_{mech} = -\sum_{x_k}^{x_v} f(x) \Delta x$$

- *Volumetric work*



$$f(x) = p(V) \cdot A_s$$

$$dW_{térf} = -p(V) A_s dx = -p(V) dV$$

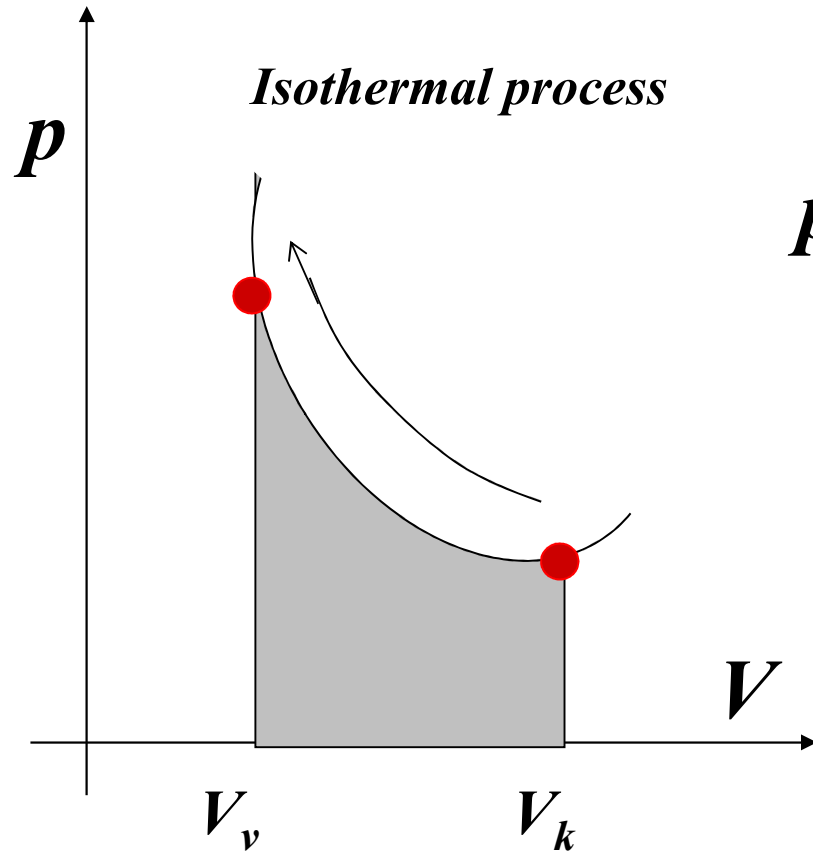
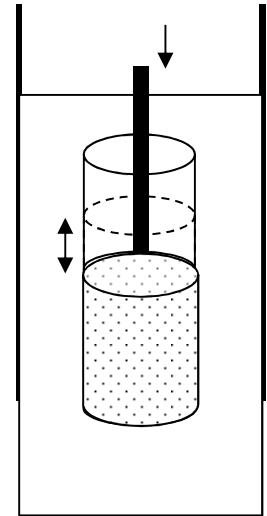
**The work is not state function!**

$$W_{mech} = -\sum_{x_k}^{x_v} p(V) \Delta V$$

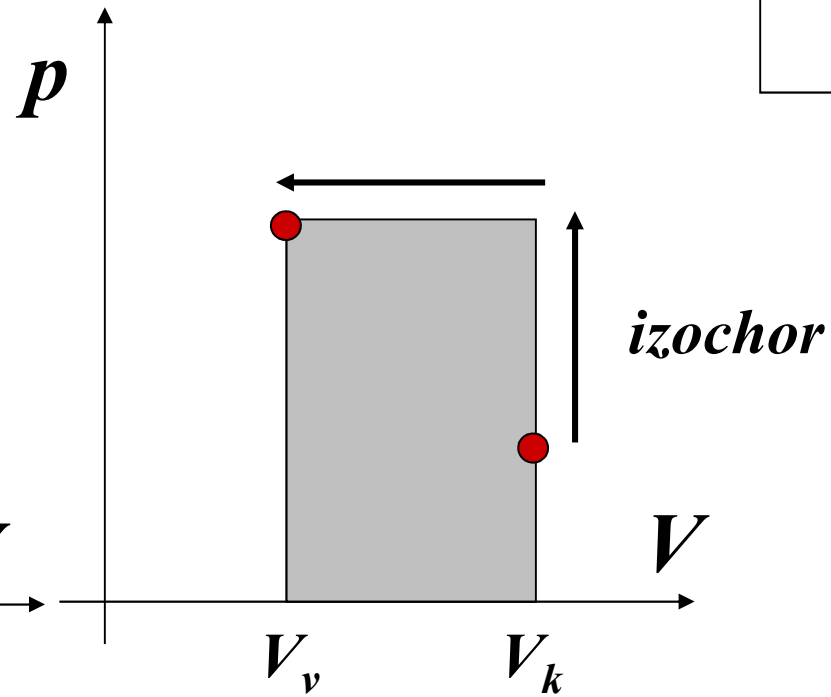
*compression:*

$$V_v < V_k$$

$$W_{vol} > 0$$

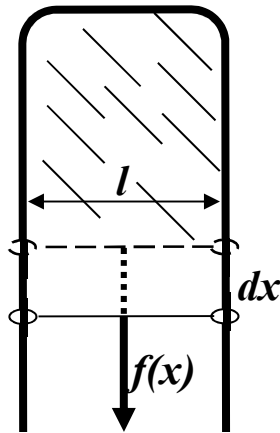


$$W = -nRT \ln \frac{V_v}{V_k}$$



$$W = -p \cdot \Delta V$$

- *Surface interaction*



$$f(x) = -2\gamma \cdot l$$

$$dW_{fel} = 2\gamma l dx = \gamma dA_s$$

$$W_{fel} = \gamma \cdot \Delta A_s$$

- *Chemical change*

$$\Delta W_{kém} = \sum_{i=1}^K \left( \frac{\Delta U}{\Delta n_i} \right) \Delta n_i = \sum_{i=1}^K \mu_i \Delta n_i$$

$\mu_i$ : chemical potential

The change of internal energy is the sum of individual energy exchanges

$$\Delta U = \sum_i \Delta W_i = \sum_i y_i \cdot \Delta x_i$$

$$\Delta U = -p\Delta V + \gamma\Delta A_s + \Phi\Delta q + \mathbf{H}\Delta\mathbf{M} + \mathbf{E}\Delta\mathbf{P} + \sum_{i=1}^K \mu_i\Delta n_i$$

volumetric

surface

electric

magnetic

electrostatic

chemical

**Where is the thermal interaction????**

# Characterization of the thermodynamic system

Macroscopic characterization: **extensive** and **intensive** variables

Extensive variables: their value is proportional to the size of the system

Intensive variables: their value is independent of the size of the system

Extensive variable	Intensive variable	Product: energy change
Volume ( $V$ ) Matter ( $n$ ) Charge ( $Q$ ) Entropy ( $S$ )	Pressure ( $p$ ) Chemical potential ( $\mu$ ) Electric potential ( $\varphi$ ) Temperature ( $T$ )	Volumetric work ( $p\Delta V$ ) Work of material transport ( $\mu\Delta n$ ) Electric work ( $\varphi\Delta Q$ ) <b>Heat ???</b>

$$\Delta U = -p\Delta V + T\Delta S$$

*more often*

$$\Delta U = -p\Delta V + T\Delta S + \Phi\Delta q + \mathbf{H}\Delta\mathbf{M} + \mathbf{E}\Delta\mathbf{P} + \sum_{i=1}^K \mu_i\Delta n_i$$

$$\Delta W_i = y_i \cdot \Delta x_i$$

$$\Delta Q = T\Delta S$$

- *Thermal interactions*

$$\Delta Q = T \Delta S$$

entropy

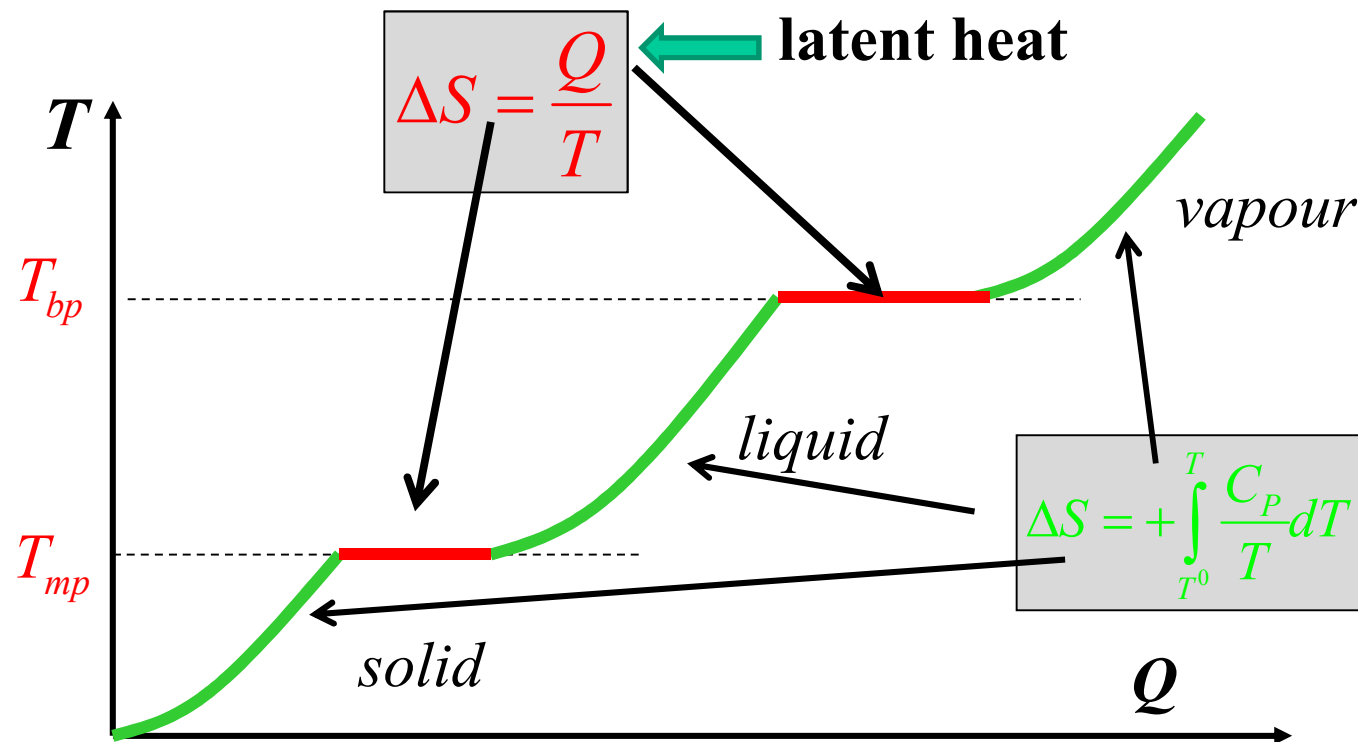
$$\Delta U = -p\Delta V + T\Delta S + \sum_{i=1}^K \mu_i \Delta n_i + \dots +$$

Chemical potential

$$\Delta Q = T \Delta S$$

Thermal interactions

*temperature changes*  
*temperature does not change*





# First law of thermodynamics

- Law of conservation of energy.
- Energy may be converted into different forms, but the total energy of the system remains constant.
- The change in the internal energy of the system is the sum of the supplied heat ( $Q_E$ ) and the work ( $W$ ) done on the system.

Work parts:

*Volumetric work*

$$W_V = -p\Delta V$$

Negative, because in the case of work done on the system  $V_2 - V_1 < 0$ .

*Electric work:*

$$W_Q = \varphi \Delta Q$$

*Material transport:*

$$W_n = \mu \Delta n$$

*Generalized:*

$$W^i = y_{\text{int}}^i \Delta x_{\text{ext}}^i$$

$$\Delta U = -p\Delta V + T\Delta S + \sum_{i=1}^K \mu_i \Delta n_i + \dots +$$

Isochoric process ( $\Delta V=0$ ):

$$\Delta E = Q_V$$

Change in internal energy is caused only by the heat exchange.

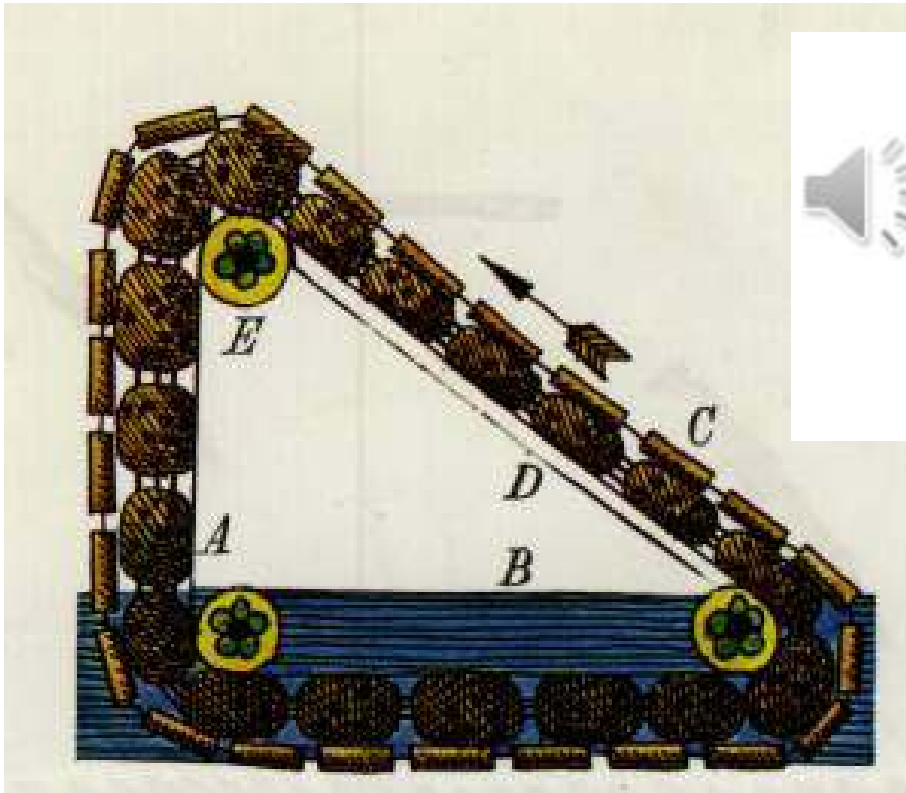
Izobaric process ( $p=\text{constant}$ ):

$$\Delta E = Q_p + W_V = Q_p - p\Delta V$$

# First law of thermodynamics



Conservation of energy → no perpetuum mobile



*Every Note*

## PERPETUUM MOBILE

*for Violin and Orchestra*

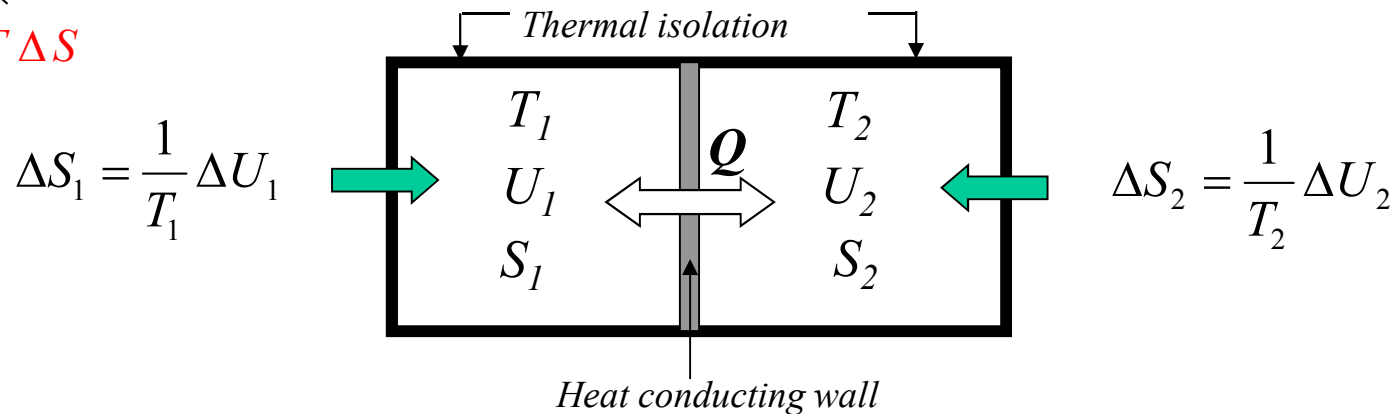
*Vivace non troppo* O. Novacek

*ff* *dim.* *sempre pp* *molto cresc.* *ff*

# Entropy change in isolated system when the temperature equalizes

$$\Delta U = -\cancel{p\Delta V} + T\Delta S$$

$$\Delta U = Q = T\Delta S$$



$$U = U_1 + U_2 = \text{állandó} \quad \Delta U = 0 \quad \Delta U_1 = -\Delta U_2$$

$$S = S_1 + S_2 = ? \quad \Delta S = \Delta S_1 + \Delta S_2 = ? \quad \Delta S = \frac{1}{T_1} \Delta U_1 + \frac{1}{T_2} \Delta U_2 = \frac{T_2 - T_1}{T_2 T_1} \cdot \Delta U_1 \neq 0$$

$$\text{ha } T_2 > T_1 \quad \text{akkor} \quad \frac{T_2 - T_1}{T_2 T_1} > 0 \quad \text{és} \quad \Delta U_1 > 0 \quad \Rightarrow \quad \Delta S > 0$$

$$\text{ha } T_2 < T_1 \quad \text{akkor} \quad \frac{T_2 - T_1}{T_2 T_1} < 0 \quad \text{és} \quad \Delta U_1 < 0 \quad \Rightarrow \quad \Delta S > 0$$

$$\text{ha } T_2 = T_1 \quad \text{akkor} \quad \frac{T_2 - T_1}{T_2 T_1} = 0 \quad \text{és} \quad \Delta U_1 = 0 \quad \Rightarrow \quad \Delta S = 0$$

**Due to temperature equalization the entropy increases!**

Entropy is an **extensive** variable.  
Is it conservative, like energy ?

## Entropy change in isolated system when the pressure equalizes

$$\Delta U = T\Delta S - p\Delta V + \sum_{i=1}^K \mu_i \Delta n_i + \dots + \quad \longrightarrow \quad \Delta S = \frac{\Delta U}{T} + \frac{p}{T} \Delta V - \sum_{i=1}^K \frac{\mu_i}{T} \Delta n_i + \dots +$$

$$\Delta S = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \Delta U_1 + \left( \frac{p_1}{T_1} - \frac{p_2}{T_2} \right) \Delta V_1 - \left( \frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) \Delta n_1$$

*Isotherm equalisation process :*

ha  $p_1 > p_2$  akkor  $\frac{p_1}{T} - \frac{p_2}{T} > 0$  és  $\Delta V_1 > 0 \quad \longrightarrow \quad \Delta S > 0$

ha  $p_1 < p_2$  akkor  $\frac{p_1}{T} - \frac{p_2}{T} < 0$  és  $\Delta V_1 < 0 \quad \longrightarrow \quad \Delta S > 0$

ha  $p_1 = p_2$  akkor  $\frac{p_1}{T} - \frac{p_2}{T} = 0$  és  $\Delta V_1 > 0 \quad \longrightarrow \quad \Delta S = 0$

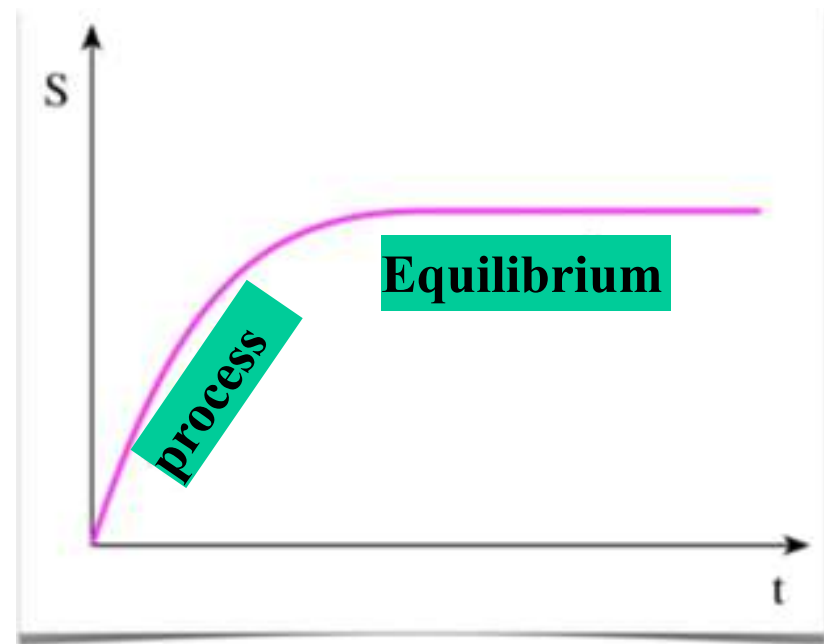
In isolated system during temperature and/or pressure equalization process the entropy increases!

# Second Law of Thermodynamics

- The entropy of an isolated system never decreases; i.e.

$$\Delta S \geq 0,$$

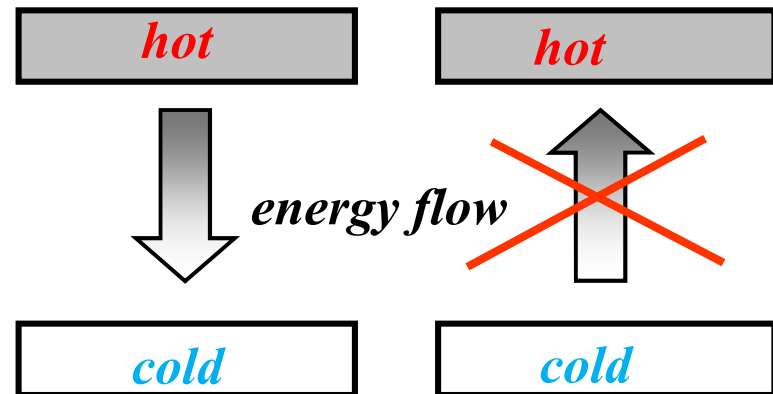
approaching equilibrium,  $S \rightarrow S_{\max}$ .



- Examples of real processes:**
  - i. temperature equalization;
  - ii. mixing of gases;
  - iii. conversion of macroscopic (ordered) KE to thermal (random) KE.

## Second law of thermodynamics

- Heat flows spontaneously from regions of high to low temperature.
- In an isolated system only such processes occur spontaneously which tend to equilibrate the respective intensive variables.
- During spontaneous processes entropy increases. Thermodynamic equilibrium is characterized by entropy maximum.
- Spontaneous processes proceed towards the most probable state.



The essentially endless heat content of oceans cannot be used to spontaneously produce useful work.

*entropy*  *arrow of time*

## Third law of thermodynamics

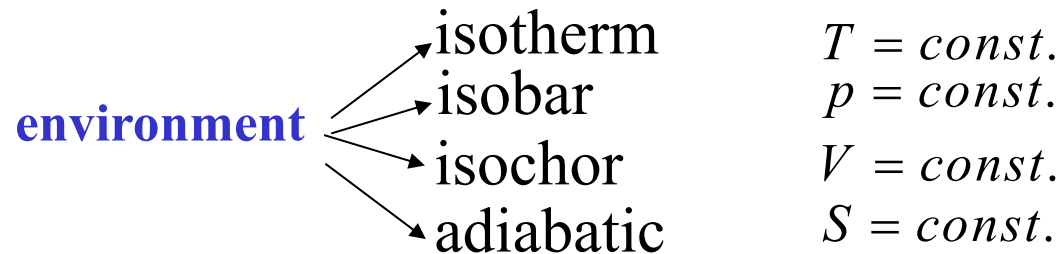
- The entropy of one-component, crystallizing material at 0 K temperature is 0.
- The 3<sup>rd</sup> Law fixes the absolute value of the entropy; i.e.  
$$S \rightarrow 0 \text{ as } T \rightarrow 0.$$

### The unattainability of absolute zero

It is impossible to reach  $T = 0$  in a finite number of steps.



## *Environmental effects*

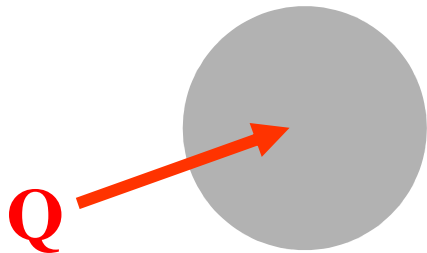


**Certain part of internal energy is devoted to maintain the constancy of environment.**

Usable energy

$\neq$

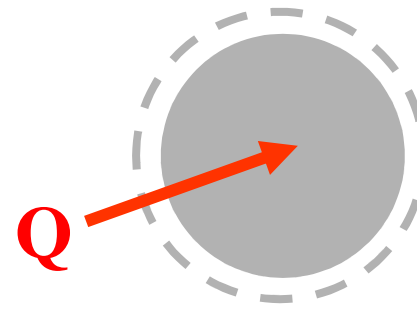
Internal energy change



$V = \text{konst.}$

$$\left( \frac{\Delta Q}{\Delta T} \right)_V < \left( \frac{\Delta Q}{\Delta T} \right)_p$$

$$C_V < C_p$$



$p = \text{konst.}$

## Useable part of internal energy at constant pressure:

In order to maintain the constancy of pressure in isobaric situation there is energy exchange with the environment.

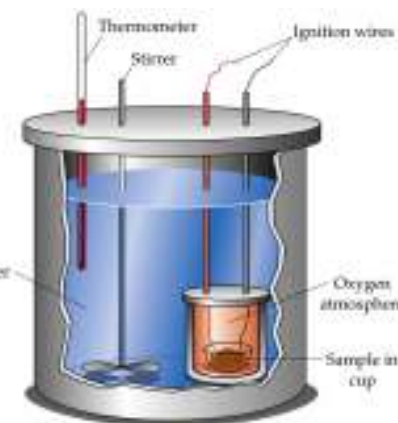
The remaining useable part of internal energy is called: **enthalpy**.

**H** enthalpy  $\rightarrow$   $H = U + pV$

$$\Delta H = \Delta U + p\Delta V$$

$$\Delta H = T\Delta S - \cancel{p\Delta V} + \cancel{p\Delta V} = T\Delta S = Q$$

*calorimeter*



$\leftarrow$  **Heat !**

The enthalpy is the useable part of internal energy at constant pressure.

$$\Delta H = Q$$

## Useable part of internal energy at constant temperature:

In order to maintain the constancy of temperature in isotherm process there is energy exchange with the environment.

The remaining useable part of internal energy is called: **free energy**

**free energy** →

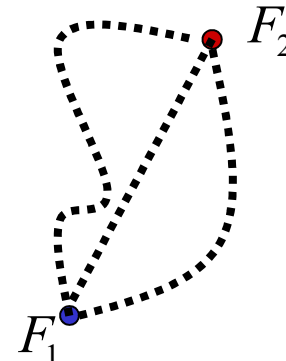
$$F = U - TS$$

**extenzív mennyiség**

$$\Delta F = \Delta U - T\Delta S$$



$$\Delta F = \cancel{T\Delta S} - p\Delta V - \cancel{T\Delta S} = -p\Delta V = W_{mech}$$



$$\Delta F = F_2 - F_1$$

The free energy is the useable part of internal energy at constant temperature.

$$\Delta F = W_{mech}$$

**Useable part of internal energy at constant temperature and pressure:**

In order to maintain the constancy of temperature and pressure of the environment, there is energy exchange with the environment.

The remaining useable part of internal energy is called: **free enthalpy** or **Gibbs free energy**.

**free enthalpy**



$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S$$

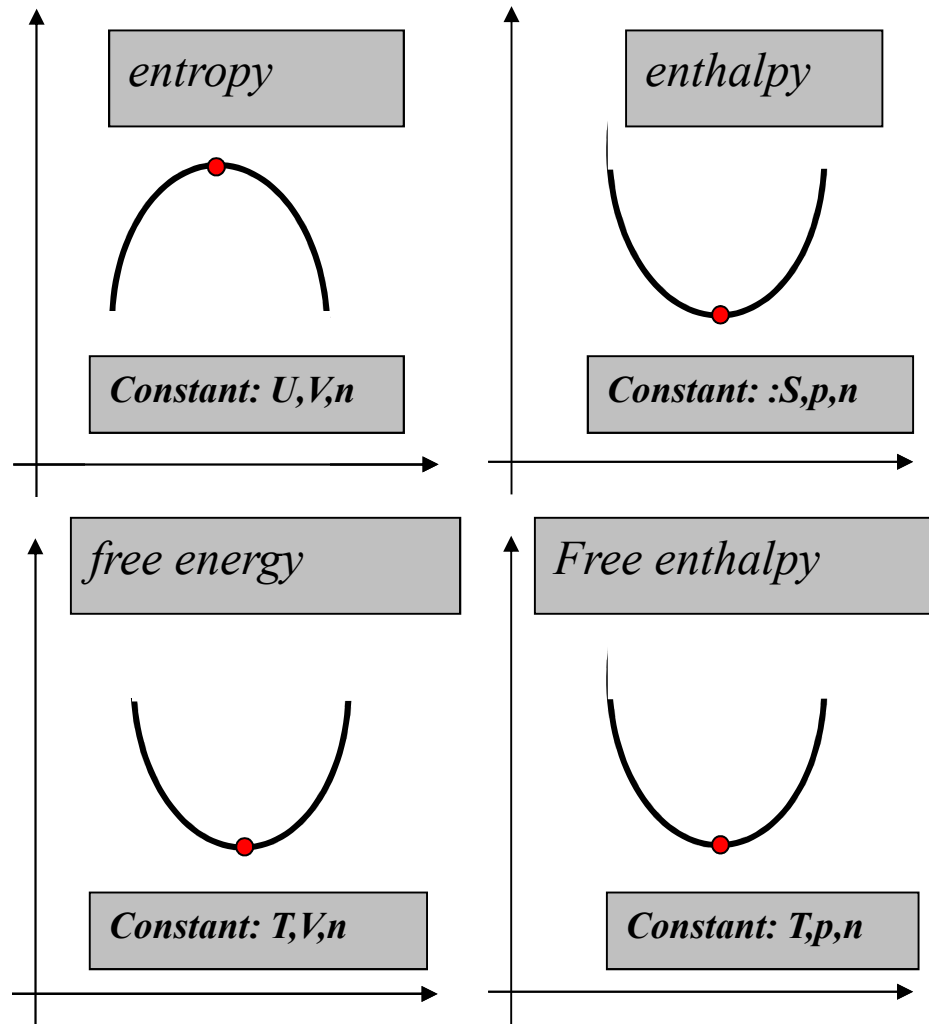


$$\Delta G = \sum_i \mu_i \Delta n_i == W_{kém}$$

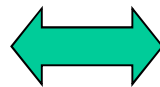


*chemical potential*

## *Conditions of thermodynamic equilibrium*



Thermodynamic equilibrium



Mathematical extremum problem